The structure of Fe-Ni alloy in Earth's inner core

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Shigehiko Tateno,[1] Kei Hirose,[1,2] Tetsuya Komabayashi,[1] Haruka Ozawa,[1,2] and Yasuo Ohishi[3]

Received 23 April 2012; revised 29 May 2012; accepted 29 May 2012; published 26 June 2012.

[1] The crystal structure of Fe-10%Ni was investigated up to 340 GPa and 4700 K, corresponding to the Earth's inner core conditions by synchrotron X-ray diffraction measurements *in-situ* at ultrahigh pressure and temperature in a laser-heated diamond-anvil cell. The results show that hexagonal closed-packed (hcp) structure is stable throughout the experimental conditions investigated with no evidence for a phase transition to body-centered cubic (bcc) or face-centered cubic (fcc) phases. The axial *c*/*a* ratio of the hcp crystal obtained around 330 GPa has a small temperature dependence similar to the axial ratio of pure Fe. Iron alloy with less than 10% Ni crystallizes to an hcp structure with *c*/*a* ratio of ∼1.61 at inner core conditions, although the effect of small amount of light elements remains to be examined by experiments. **Citation:** Tateno, S., K. Hirose, T. Komabayashi, H. Ozawa, and Y. Ohishi (2012), The structure of Fe-Ni alloy in Earth's inner core, *Geophys. Res. Lett.*, *39*, L12305, doi:10.1029/2012GL052103.

1. Introduction

[2] The liquid core crystallizes to form the solid inner core with structural complexity, which is evident from seismic anisotropy with both hemispherical and depth variations [*Morelli et al.*, 1986; *Woodhouse et al.*, 1986; *Tanaka and Hamaguchi*, 1997; *Song and Helmberger*, 1998]. It is generally believed that such seismic anisotropy results from the lattice-preferred orientation of an iron alloy comprising the inner core [*Stixrude and Cohen*, 1995a].

[3] The crystal structure of iron alloy is essential for deciphering the seismic observations, and thus, understanding the core dynamics. The stable form of pure iron under very high pressure and temperature (*P-T*) conditions has long been a matter of debate. While bcc [*Belonoshko et al.*, 2003], fcc [*Mikhaylushkin et al.*, 2007], and stacking-disordered phases [*Ishikawa et al.*, 2011] have been proposed in addition to an hcp phase [*Stixrude and Cohen*, 1995b], very recent laser-heated diamond-anvil cell (DAC) experiments performed by *Tateno et al.* [2010] revealed that iron adopts the hcp structure up to 377 GPa and 5700 K under inner core *P-T* conditions.

[4] The effect of impurity element(s) on the stable crystal structure still remains controversial. Based on geochemical consideration, it is thought that the Earth's core includes ∼5 wt.% Ni [*McDonough and Sun*, 1995]. Experiments by *Mao et al.* [1990] reported the hcp $Fe_{0.8}Ni_{0.2}$ alloy to 260 GPa at ambient temperature. Subsequent laser-heated DAC experiments demonstrated that hcp Fe-18.4 wt.% Ni is stable to at least 278 GPa at 2000 K [*Kuwayama et al.*, 2008]. More recent DAC studies by *Sakai et al.* [2011] also showed hcp Fe-10%Ni up to 250 GPa at 2730 K. The stability of hcp $Fe_{0.9}Ni_{0.1}$ under inner core conditions is supported by *ab-initio* calculations as well [*Ekholm et al.*, 2011]. In contrast, experiments performed by *Dubrovinsky et al.* [2007] reported a phase transition in $Fe_{0.9}Ni_{0.1}$ from hcp to bcc above 225 GPa and 3400 K. Since nickel is a fcc stabilizer, it expands the stability of fcc relative to hcp [*Lin et al.*, 2002; *Mao et al.*, 2006; *Kuwayama et al.*, 2008; *Komabayashi et al.*, 2012]. Here we conducted ultrahigh *P-T* experiments on Fe-10%Ni as a plausible inner core material using the laser-heated DAC techniques. Based on the *in-situ* X-ray diffraction (XRD) measurements, the crystal structure of the stable phase was identified up to 340 GPa and 4700 K.

2. Experimental Techniques

[5] High *P-T* conditions were generated using laser-heated DAC techniques. We used Fe-10 wt.% Ni foil (>99.99% purity, *Rare Metallic*) as a starting material. It was loaded into a hole in a pre-indented rhenium gasket between the SiO_2 glass pellets used as a pressure medium and a thermal insulator. The samples within the DAC were dried at 393 K for >1 h in a vacuum oven. Argon gas was introduced to flush the sample when the oven was opened. The sample was then compressed to high pressure in an argon atmosphere in a glove box. Double-beveled diamond anvils with either 40 or 60 μm culets were used, and therefore, sample size was limited to 20–25 μm in diameter.

[6] Angle-dispersive XRD measurements were conducted at BL10XU, SPring-8 [*Ohishi et al.*, 2008]. The XRD patterns were collected *in-situ* at high *P-T* on a CCD detector (*Bruker APEX*) with a typical exposure time of 10 sec. A monochromatic incident X-ray beam was focused by stacked compound refractive lenses and collimated to approximately 6-μm area (full-width of half maximum) on the sample. The wavelengths used were 0.4178(4), 0.4227(6), 0.4188(6), and 0.4114(3) (∼30 keV) in runs #1 through #4, respectively. Visible fluorescence light from diamond excited by X-rays was used to precisely align the laser-heated spot with the X-ray beam. Two-dimensional XRD images were integrated as a function of two-theta angle in order to produce conventional one-dimensional diffraction pattern using the IP Analyzer program [*Seto et al.*, 2010].

[1]Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo, Japan.
[2]Institute for Research on Earth Evolution, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan.
[3]Japan Synchrotron Radiation Research Institute, Hyogo, Japan.

Corresponding author: S. Tateno, Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan. (tateno.s.aa@m.titech.ac.jp)

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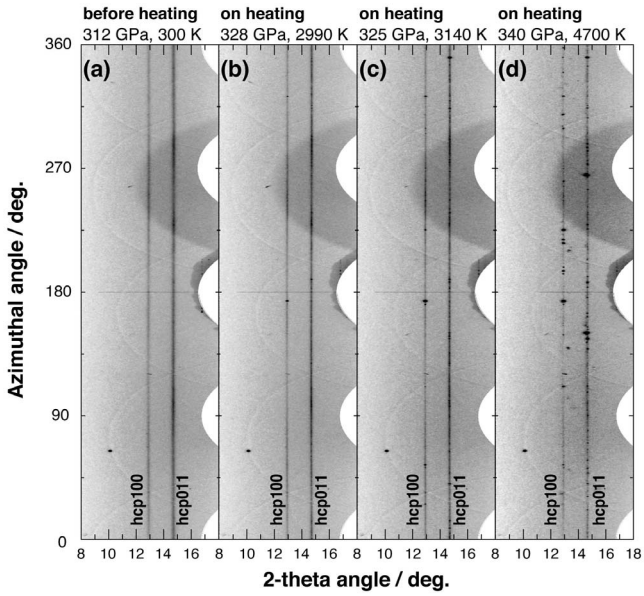

Figure 1. Unrolled XRD images of hcp Fe-10%Ni. Broad diffraction lines at 312 GPa (a) before heating became sharp within 2 min, (b) after laser heating. (c) At a constant temperature of ~3000 K, Debye rings from the hcp phase became spotty with time. (d) More spotty but still continuous rings were observed at 4700 K.

[7] Heating was performed from both sides of the sample by employing two 100 W single mode Yb fiber lasers (*SPI*). This minimizes axial temperature gradients. The laser-heated spot was 15 to 20 μm across. Temperature was measured by the spectroradiometric method. We used beam shapers (*New focus*) to reduce radial temperature gradients in the sample. These convert a beam with a Gaussian intensity distribution to the one with a flat-top distribution. Sample temperatures reported are the average temperatures in the 6 μm region probed by X-rays across the hot spot. Temperature variations within this 6 μm spot were less than 10% (Figure S1 in the auxiliary material).[1]

[8] An internal pressure standard was not used in the present experiments in order to avoid possible chemical reaction with the sample. Alternatively, we determined the sample pressure from the unit-cell volume of hcp Fe-10%Ni with the peaks of 100 and 011 reflections using its *P-V-T* (*V* is volume) equation of state [*Komabayashi et al.*, 2012]. We considered $\pm$10% uncertainty in temperature, leading to about $\pm$2% errors in pressure (for example, 340 $\pm$ 6 GPa at 4700 K).

3. Crystal Structure of the Fe-Ni Alloy

[9] We performed four separate sets of experiments at pressures between 248 and 340 GPa and temperatures up to 4700 K. In the first set of experiments using the diamond anvils with 40 μm culet, the starting material was first compressed to 312 GPa at room temperature. The corresponding XRD pattern included broad peaks only from hcp Fe-10%Ni (Figures 1a and 2a). We then heated the sample to 2990 K at 328 GPa and observed that diffraction lines from the hcp phase became sharper. In addition, several spots appeared on the Debye rings after heating for 2 min (Figure 1b), indicating grain growth and thus the stability of hcp at this *P-T* condition. With further heating to ~3000 K, the diffraction rings from the hcp phase became more spotty with time (Figure 1c). When the sample temperature was increased to 4700 K at 340 GPa, the diffraction peaks from the hcp phase became very spotty although the Debye rings were still continuous (Figures 1d and 2b). Diffraction lines from other phases such as bcc and fcc structures were not found in any of the XRD patterns. Two additional experiments (runs #2 and #3) were performed at 314–332 GPa and 1780–4030 K. The hcp phase was also found to be stable in these runs just as it was in run #1. SiO_2 phases were not observed in any of these experiments although we used SiO_2 glass as a pressure medium and a thermal insulator. Note that crystallization from SiO_2 glass is quite sluggish even at low pressure [*Komabayashi et al.*, 2012] and even more sluggish above 300 GPa [*Tateno et al.*, 2010].

[10] The fourth experiment was carried out at the relatively low pressures of 248–256 GPa and 2470–3610 K using 60 μm-culet anvils. This run aimed to reproduce the earlier experimental results by *Dubrovinsky et al.* [2007], who reported the phase transition from hcp to bcc structure in $Fe_{0.9}Ni_{0.1}$ above 225 GPa and 3400 K. More recent experimental study by *Sakai et al.* [2011] found that hcp $Fe_{0.9}Ni_{0.1}$ was stable up to 250 GPa and 2730 K, although temperatures examined were lower than those by *Dubrovinsky et al.* [2007]. Our results demonstrate that the diffraction peaks from the hcp phase became spotty during heating, which again indicates the stability of this structure at these P-T conditions. The source of discrepancy is not clear. The only difference is a pressure medium; they used $Mg_{0.87}Fe_{0.13}O$, while we employed SiO_2 glass. However, it is unlikely that such difference affected the stable crystal structure.

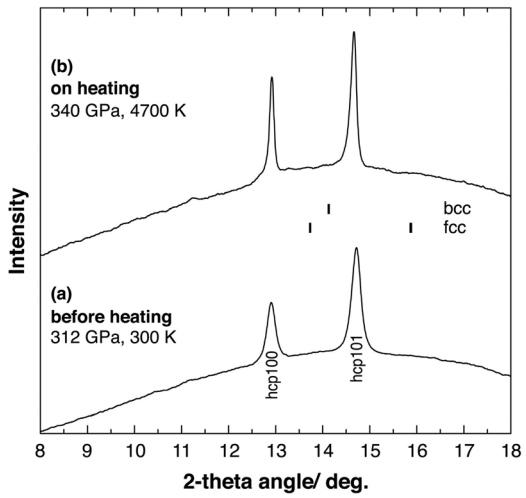

Figure 2. Representative integrated XRD patterns of hcp Fe-10%Ni at (a) 312 GPa before heating and (b) 340 GPa and 4700 K. Peak positions of the fcc and bcc structures were calculated for volumes larger by 0 to 1% than that of observed hcp phase. λ = 0.4178(4) Å.

[1]Auxiliary materials are available in the HTML. doi:10.1029/2012GL052103.

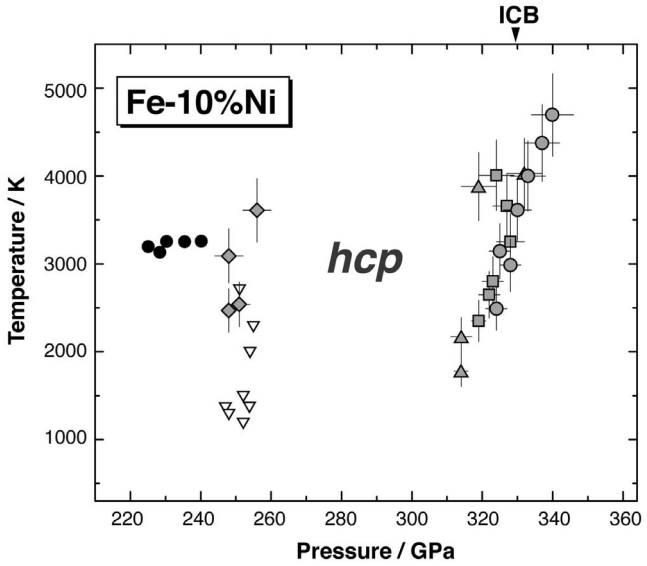

Figure 3. Phase diagram of Fe-10%Ni. The hcp phase is stable under inner core conditions. Four separate experiments were carried out as shown by different gray symbols. Previous experimental data showing the stability of hcp phase by *Sakai et al.* [2011] are also plotted (open triangle). The bcc phase was observed by *Dubrovinsky et al.* [2007] (black circle). The locations of inner-core boundary (ICB) are indicated with arrowheads.

[11] These results are summarized in Figure 3 and Table S1. The stability of hcp Fe-10%Ni was confirmed to 340 GPa and 4700 K corresponding to the inner core conditions. We observed no evidence for a phase transition to bcc or fcc phase over the *P-T* range investigated. Therefore the hcp phase is a likely constituent of the Earth's inner core, but the effect of light elements (H, C, O, Si, S) on a stable crystal structure remains to be examined experimentally [*Vočadlo et al.*, 2003; *Côté et al.*, 2008].

[12] In our previous laser-heated DAC experiments on pure Fe using finely powdered iron as a starting material [*Tateno et al.*, 2010], diffractions peaks from Fe_3C were found, which indicated a contamination by carbon from the diamond anvils during laser heating [*Prakapenka et al.*, 2003]. However, in the present experiments only the hcp phase was observed to 4700 K at 340 GPa, suggesting that the contamination by carbon, if any, was limited to the surface of the iron foil. *Lord et al.* [2009] reported that the maximum solubility of carbon in solid iron is less than 0.6% at 44 GPa and decreases with increasing pressure. These suggest that the stability of the hcp phase observed in the present experiments is not affected by carbon contamination.

4. Axial Ratio of the hcp Phase

[13] Seismic waves travel 3–4% faster along the polar axis than in the equatorial plane [e.g., *Morelli et al.*, 1986; *Woodhouse et al.*, 1986]. This is usually attributed to the preferred orientation of the iron crystal with anisotropic elastic properties. Previous theoretical studies calculated the elasticity of hcp iron at inner core *P-T* conditions and discussed the origin of such seismic anisotropy [*Stixrude and Cohen*, 1995a, 1995b; *Steinle-Neumann et al.*, 2001; *Sha and Cohen*, 2006; *Vočadlo et al.*, 2009]. Knowledge of the lattice parameters is important to such calculations [*Vočadlo et al.*, 2009; *Sha and Cohen*, 2010].

[14] Here we determined the *c*/*a* axial ratio of hcp Fe-10% Ni at 314–340 GPa (Figure 4 and Table S1). The results indicate the *c*/*a* ratio of 1.615 at 4700 K and 340 GPa, which is lower than the ideal value for an hcp crystal (1.63). The ratio increased with increasing temperature, but the temperature effect is small. These data are in good agreement with results reported by *Sakai et al.* [2011] who collected data at 250 GPa. The earlier data on Fe-10%Ni at 86 GPa by *Lin et al.* [2002] indicate slightly higher values, but this can be explained by the pressure effect [*Tateno et al.*, 2010]. Compared with our previous data on pure iron at ~330 GPa [*Tateno et al.*, 2010], the present results on Fe-10%Ni alloy obtained at the same pressure range show a higher *c*/*a* ratio, indicating that incorporation of nickel increases this ratio.

[15] The *c*/*a* axial ratio has been repeatedly calculated by theory for pure iron, but the results are contradictory. The computational studies by *Steinle-Neumann et al.* [2001] and *Belonoshko et al.* [2003] reported strong temperature dependence, whereas more recent calculations show the temperature effect on the *c*/*a* ratio to be much smaller [*Gannarelli et al.*, 2005; *Sha and Cohen*, 2010] (Figure 4). Our experimental data on both pure Fe and Fe-10%Ni alloy are consistent with the latest computations.

[16] Recent calculations also suggest that elastic anisotropy of hcp iron becomes smaller with increasing temperature, even with non-ideal *c*/*a* axial ratio. If true, this would not explain the observed seismic anisotropy [*Vočadlo et al.*, 2009; *Sha and Cohen*, 2010]. Nevertheless, *Tsuchiya and Fujibuchi* [2009] showed that the incorporation of silicon into iron enhances the elastic anisotropy of the hcp phase at core pressures. We suggest that the minor light element may

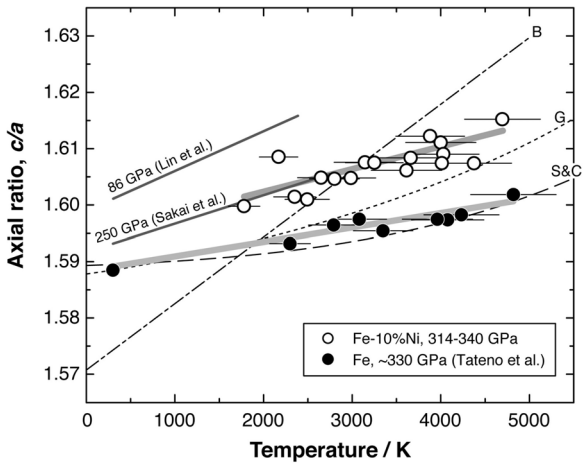

Figure 4. Axial ratios (*c*/*a*) of hcp Fe-10%Ni alloy and pure Fe. Open circles, Fe-10%Ni at 314–340 GPa from this study; solid circles, pure Fe at ~330 GPa from *Tateno et al.* [2010]. Heavy lines indicate the linear fits to the experimental data presented in this study. Thin lines indicate previous experimental data on Fe-10%Ni; L, *Lin et al.* [2002] at 86 GPa; S, *Sakai et al.* [2011] at 250 GPa. Results of theoretical calculations for pure Fe at constant atomic volumes are also shown. S&C, *Sha and Cohen* [2006] for 7.4 $Å^3$; G, *Gannarelli et al.* [2005] for 7.0 $Å^3$; B, *Belonoshko et al.* [2003] for 7.2 $Å^3$.

be the key to understand the origin of strong inner core anisotropy.

5. Summary and Conclusion

[17] We have performed synchrotron XRD measurements of Fe-10%Ni alloy at ultrahigh *P-T* conditions up to 340 GPa and 4700 K by using laser-heated DAC techniques. Hcp is a stable form of Fe-10%Ni in the inner core. The axial *c*/*a* ratio of the hcp crystal is ∼1.61. Small amount of light element is likely present in the inner core, whose effect on crystal structure remains to be examined by experiments.

[18] **Acknowledgments.** We thank N. Hirao for his technical assistance. The synchrotron X-ray diffraction measurements were conducted at BL10XU of SPring-8 (proposals 2010B0087 and 2011A0087). This research was supported by the Global Center-of-Excellence program "From the Earth to Earths."

[19] The Editor thanks the two anonymous reviewers for assisting in the evaluation of this paper.

References

Belonoshko, A. B., R. Ahuja, and B. Johansson (2003), Stability of the body-centered-cubic phase of iron in the Earth's inner core, *Nature*, *424*, 1032–1034, doi:10.1038/nature01954.

Côté, A. S., L. Vočadlo, and J. P. Brodholt (2008), Light elements in the core: Effects of impurities on the phase diagram of iron, *Geophys. Res. Lett.*, *35*, L05306, doi:10.1029/2007GL032788.

Dubrovinsky, L., et al. (2007), Body-centered cubic iron-nickel alloy in Earth's core, *Science*, *316*, 1880–1883, doi:10.1126/science.1142105.

Ekholm, M., A. S. Mikhaylushkin, S. I. Simak, B. Johansson, and I. A. Abrikosov (2011), Configurational thermodynamics of Fe-Ni alloys at Earth's core conditions, *Earth Planet. Sci. Lett.*, *308*, 90–96, doi:10.1016/j.epsl.2011.05.035.

Gannarelli, C. M. S., D. Alfe, and M. J. Gillan (2005), The axial ratio of hcp iron at the conditions of the Earth's inner core, *Phys. Earth Planet. Inter.*, *152*, 67–77, doi:10.1016/j.pepi.2005.06.003.

Ishikawa, T., T. Tsuchiya, and J. Tsuchiya (2011), Stacking-disordered phase of iron in the Earth's inner core from first principles, *Phys. Rev. B*, *83*, 212101, doi:10.1103/PhysRevB.83.212101.

Komabayashi, T., K. Hirose, and Y. Ohishi (2012), In situ X-ray diffraction measurements of the fcc–hcp phase transition boundary of an Fe–Ni alloy in an internally heated diamond anvil cell, *Phys. Chem. Miner.*, *39*, 329–338, doi:10.1007/s00269-012-0490-3.

Kuwayama, Y., K. Hirose, N. Sata, and Y. Ohishi (2008), Phase relations of iron and iron–nickel alloys up to 300 GPa: Implications for composition and structure of the Earth's inner core, *Earth Planet. Sci. Lett.*, *273*, 379–385, doi:10.1016/j.epsl.2008.07.001.

Lin, J. F., D. L. Heinz, A. J. Campbell, J. M. Devine, W. L. Mao, and G. Shen (2002), Iron-nickel alloy in the Earth's core, *Geophys. Res. Lett.*, *29*(10), 1471, doi:10.1029/2002GL015089.

Lord, O. T., M. J. Walter, R. Dasgupta, D. Walker, and S. M. Clark (2009), Melting in the Fe-C system to 70 GPa, *Earth Planet. Sci. Lett.*, *284*, 157–167, doi:10.1016/j.epsl.2009.04.017.

Mao, H. K., Y. Wu, L. C. Chen, J. F. Shu, and A. P. Jephcoat (1990), Static compression of iron to 300 GPa and $Fe_{0.8}Ni_{0.2}$ alloy to 260 GPa: Implications for composition of the core, *J. Geophys. Res.*, *95*(B13), 21,737–21,742, doi:10.1029/JB095iB13p21737.

Mao, W. L., A. J. Campbell, D. L. Heinz, and G. Y. Shen (2006), Phase relations of Fe-Ni alloys at high pressure and temperature, *Phys. Earth Planet. Inter.*, *155*, 146–151, doi:10.1016/j.pepi.2005.11.002.

McDonough, W. F., and S. Sun (1995), The composition of the Earth, *Chem. Geol.*, *120*, 223–253, doi:10.1016/0009-2541(94)00140-4.

Mikhaylushkin, A. S., S. I. Simak, L. S. Dubrovinsky, N. A. Dubrovinskaia, B. Johansson, and I. A. Abrikosov (2007), Pure iron compressed and heated to extreme conditions, *Phys. Rev. Lett.*, *99*, 165505, doi:10.1103/PhysRevLett.99.165505.

Morelli, A., A. M. Dziewonski, and J. H. Woodhouse (1986), Anisotropy of the inner core inferred from *PKIKP* travel times, *Geophys. Res. Lett.*, *13*(13), 1545–1548, doi:10.1029/GL013i013p01545.

Ohishi, Y., N. Hirao, N. Sata, K. Hirose, and M. Takata (2008), Highly intense monochromatic X-ray diffraction facility for high-pressure research at SPring-8, *High Pressure Res.*, *28*, 163–173, doi:10.1080/08957950802208910.

Prakapenka, V. B., G. Shen, and L. S. Dubrovinsky (2003), Carbon transport in diamond anvil cells, *High Temp. High Pressures*, *35–36*, 237–249, doi:10.1068/htjr098.

Sakai, T., E. Ohtani, N. Hirao, and Y. Ohishi (2011), Stability field of the hcp-structure for Fe, Fe-Ni, and Fe-Ni-Si alloys up to 3 Mbar, *Geophys. Res. Lett.*, *38*, L09302, doi:10.1029/2011GL047178.

Seto, Y., D. Nishio-Hamane, T. Nagai, and N. Sata (2010), Development of a software suite on X-ray diffraction experiments, *Rev. High Pressure Sci. Technol.*, *20*, 269–276, doi:10.4131/jshpreview.20.269.

Sha, X., and R. E. Cohen (2006), Thermal effects on lattice strain in ε-Fe under pressure, *Phys. Rev. B*, *74*, 064103, doi:10.1103/PhysRevB.74.064103.

Sha, X., and R. E. Cohen (2010), Elastic isotropy of ε-Fe under Earth's core conditions, *Geophys. Res. Lett.*, *37*, L10302, doi:10.1029/2009GL042224.

Song, X. D., and D. V. Helmberger (1998), Seismic evidence for an inner core transition zone, *Science*, *282*, 924–927, doi:10.1126/science.282.5390.924.

Steinle-Neumann, G., L. Stixrude, R. E. Cohen, and O. Gulseren (2001), Elasticity of iron at the temperature of the Earth's inner core, *Nature*, *413*, 57–60, doi:10.1038/35092536.

Stixrude, L., and R. E. Cohen (1995a), High-pressure elasticity of iron and anisotropy of Earth's inner core, *Science*, *267*, 1972–1975, doi:10.1126/science.267.5206.1972.

Stixrude, L., and R. E. Cohen (1995b), Constraints on the crystalline structure of the inner core: Mechanical instability of BCC iron at high pressure, *Geophys. Res. Lett.*, *22*, 125–128, doi:10.1029/94GL02742.

Tanaka, S., and H. Hamaguchi (1997), Degree one heterogeneity and hemispherical variation of anisotropy in the inner core from *PKP*(BC)-*PKP*(DF) times, *J. Geophys. Res.*, *102*, 2925–2938, doi:10.1029/96JB03187.

Tateno, S., K. Hirose, Y. Ohishi, and Y. Tatsumi (2010), The structure of iron in Earth's inner core, *Science*, *330*, 359–361, doi:10.1126/science.1194662.

Tsuchiya, T., and M. Fujibuchi (2009), Effects of Si on the elastic property of Fe at Earth's inner core pressures: First principles study, *Phys. Earth Planet. Inter.*, *174*, 212–219, doi:10.1016/j.pepi.2009.01.007.

Vočadlo, L., D. Alfé, M. J. Gillan, I. G. Wood, J. P. Brodholt, and G. D. Price (2003), Possible thermal and chemical stabilization of body-centered-cubic iron in the Earth's core, *Nature*, *424*, 536–539, doi:10.1038/nature01829.

Vočadlo, L., D. P. Dobson, and I. G. Wood (2009), Ab initio calculations of the elasticity of hcp-Fe as a function of temperature at inner-core pressure, *Earth Planet. Sci. Lett.*, *288*, 534–538, doi:10.1016/j.epsl.2009.10.015.

Woodhouse, J. H., D. Giardini, and X.-D. Li (1986), Evidence for inner core anisotropy from free oscillations, *Geophys. Res. Lett.*, *13*, 1549–1552, doi:10.1029/GL013i013p01549.